

Practitioner's Docket No. 6171-7

CHAPTER II

Preliminary Classification:

Proposed Class:

Subclass:

TRANSMITTAL LETTER  
TO THE UNITED STATES ELECTED OFFICE (EO/US)  
(ENTRY INTO U.S. NATIONAL PHASE UNDER CHAPTER II)

|                               |                           |                          |
|-------------------------------|---------------------------|--------------------------|
| EP00/07503                    | 03 August 2000 (3.08.00)  | 06 August 1999 (6.08.99) |
| International Application No. | International Filing Date | Priority Date Claimed    |

TITLE OF INVENTION: METHOD FOR PRODUCING IMPROVED COLD-ROLLED STRIP THAT IS CAPABLE OF BEING DEEP-DRAWN OR IRONED, AND COLD-ROLLED STRIP, PREFERABLY USED FOR PRODUCING CYLINDRICAL CONTAINERS AND, IN PARTICULAR, BATTERY CONTAINERS

APPLICANT(S): Hille & Mueller GmbH; PFEIFENBRING, Karlfried; STEINMANN, Hans-Guenter; SCHMIDT, Ferdinand; OLBERDING, Werner; and RUBART, Marcel Sebastian

Box PCT  
Assistant Commissioner for Patents  
Washington D.C. 20231  
ATTENTION: EO/US

---

CERTIFICATION UNDER 37 C.F.R. ' 1.8(a) and 1.10\*  
(When using Express Mail, the Express Mail label number is **mandatory**;  
Express Mail certification is optional.)

I hereby certify that, on the date shown below, this correspondence is being:

MAILING

G deposited with the United States Postal Service in an envelope addressed to the Assistant Commissioner for Patents, Washington D.C. 20231  
37 C.F.R. § 1.8(a)

G with sufficient postage as first class mail.

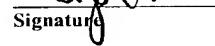
G as "Express Mail Post Office to Addressee"

Mailing Label No. EL 829634412US (mandatory)

TRANSMISSION

G facsimile transmitted to the Patent and Trademark Office, (703) \_\_\_\_\_

Date: 5 Feb. 2002



Signature

Stephen L. Grant  
(type or print name of person certifying)

\* Only the date of filing (' 1.6) will be the date used in a patent term adjustment calculation, although the date on any certificate of mailing or transmission under ' 1.8 continues to be taken into account in determining timeliness. See ' 1.703(j). Consider "Express Mail Post Office to Addressee" (' 1.10) or facsimile transmission (' 1.6(d)) for the reply to be accorded the earliest possible filing date for patent term adjustment calculations

1. Applicant herewith submits to the United States Elected Office (EO/US) the following items under 35 U.S.C. § 371:
  - a. This express request to immediately begin national examination procedures (35 U.S.C. § 371(f)).
  - b. The U.S. National Fee (35 U.S.C. § 371(c)(1)) and other fees (37 C.F.R. § 1.492) as indicated below:

2. Fees

| CLAIMS FEE*  | (1) FOR   | (2) NUMBER FILED | (3) NUMBER EXTRA            | (4) RATE     | (5) CALCULATIONS |
|--------------|---|------------------|-----------------------------|--------------|------------------|
|              | TOTAL CLAIMS  | 79 -20 =         | 59                          | x \$18.00 =  | \$1,062.00       |
|              | INDEPENDENT CLAIMS  | 3 - 3 =          | 0                           | x \$84.00 =  | \$0.00           |
|              | MULTIPLE DEPENDENT CLAIM(S) (if applicable)   |                  |                             | + \$280.00   | \$0.00           |
| BASIC FEE    | U.S. PTO WAS NOT INTERNATIONAL PRELIMINARY EXAMINATION AUTHORITY<br>Where no international preliminary examination fee as set forth in § 1.482 has been paid to the U.S. PTO, and payment of an international search fee as set forth in Section 1.445(a)(2) to the U.S. PTO:<br>where a search report on the international application has been prepared by the European Patent Office or the Japanese Patent Office (37 C.F.R. § 1.492(a)(5)) ..... |                  |                             |              | \$890.00         |
|              |   |                  | Total of above Calculations | = \$1,952.00 |                  |
| SMALL ENTITY | Reduction by 1/2 for filing by small entity, if applicable. Assertion must be made. (note 37 C.F.R. § 1.27)   |                  |                             | - \$0.00     |                  |
|              |   |                  | Subtotal                    | \$1,952.00   |                  |
|              |   |                  | Total National Fee          | \$1,952.00   |                  |
| TOTAL        |   |                  | Total Fees enclosed         | \$1,952.00   |                  |

Attached is a check in the amount of \$1,952.00.

A duplicate copy of this sheet is enclosed.

3. A copy of the International application as filed (35 U.S.C. § 371(c)(2)) has been transmitted by the International Bureau.

Date of mailing of the application (from form PCT/IB/308): not known.

4. A translation of the International application into the English language (35 U.S.C. § 371(c)(2)) is transmitted herewith.

5. Amendments to the claims of the International application under PCT Article 19 (35 U.S.C. § 371(c)(3)) are transmitted herewith.

6. A translation of the amendments to the claims under PCT Article 19 (38 U.S.C. § 371(c)(3)) is transmitted herewith.

7. A copy of the international examination report (PCT/IPEA/409) Transmitted herewith

8. Annex(es) to the international preliminary examination report is/are transmitted herewith.

9. A translation of the annexes to the international preliminary examination report is transmitted herewith.

10. An unexecuted oath or declaration of the inventor (35 U.S.C. § 371(c)(4)) complying with 35 U.S.C. § 115 is submitted herewith, and such oath or declaration identifies the application and any amendments under PCT Article 19 that were transmitted as stated in points 3(b) or 3(c) and 5(b); and states that they were reviewed by the inventor as required by 37 C.F.R. § 1.70.

II. Other document(s) or information included:

11. An International Search Report (PCT/ISA/210) or Declaration under PCT Article 17(2)(a) has been transmitted by the International Bureau.

Date of mailing (from form PCT/IB/308): not known.

12. An Information Disclosure Statement under 37 C.F.R. §§ 1.97 and 1.98 will be transmitted within THREE MONTHS of the date of submission of requirements under 35 U.S.C. § 371(c).

13. An assignment document will be transmitted later for recording. This assignment will be to Hille & Mueller GmbH, as Hille & Mueller GmbH & Co. has officially changed its corporate name since the filing date of the international application.

14. Additional documents:

- a. International Publication No. 01/11114
  - i. Specification, claims and drawing
- b. Preliminary amendment (37 C.F.R. § 1.121), with substitute specification.

15. The above items are being transmitted before 30 months from any claimed priority date.



Stephen L. Grant  
Hahn Loeser & Parks LLP  
1225 W. Market St.  
Akron, OH 44313  
USA

Attorney's Docket 6171-7

**IN THE UNITED STATES PATENT AND TRADEMARK OFFICE**

Applicant: Pfeifenbring, et al

Examiner:

Ser. No.:

Art Group:

Title: METHOD FOR PRODUCING IMPROVED COLD ROLLED BAND THAT IS CAPABLE OF BEING DEEP-DRAWN OR IRONED, AND COLD ROLLED BAND, PREFERABLY USED FOR PRODUCING CYLINDRICAL CONTAINERS AND, IN PARTICULAR, BATTERY CONTAINERS

Filed: 5 February 2002

Date: 5 February 2002

**PRELIMINARY AMENDMENT**

This Preliminary Amendment is filed as a part of the national stage entry of PCT application EP00/07503, which was filed on 3 August 2000, which is in turn based on German application 199 37 271.3, filed on 6 August 1999. The fees for the claims should be calculated based on the claims remaining after the entry of this Preliminary Amendment, which results in 79 total and 3 independent claims. Consistent with the modifications to 37 CFR §1.125, the applicant has provided a substitute specification instead of a clean copy of the paragraphs and claims as they stand after amendment.

Amendments to the Disclosure

The substitute specification has been altered from the literal translation document received to delete information above the title, to insert headings according to US practice, and to insert paragraph numbering in lieu of line numbering. These changes do not introduce new matter.

Amendments to the Claims

After the heading "CLAIMS" and before the beginning of the claims, please insert the words: -- What is claimed is: --

Please amend the claims as follows:

1. (amended) A method for producing improved cold band suitable for drawing or ironing process, with a carbon content of less than 0.5 weight percent, said cold band having two surfaces, the method comprising the steps of:

rolling [during which] the cold band [rolled] under a cold-rolling ratio of at least 30% and less than 95% [30 to 95%] ; [is subjected]

annealing the cold band by [to] a thermal treatment in an annealing furnace ; and coating the cold band [to a coating procedure, preferably on galvanic basis,] on at least one of the [its] surfaces, [where the simple or multiple-layer coating contains the elements of nickel / cobalt / iron / bismuth / indium / palladium / gold or their alloys,]

wherein the annealing step [characterized in that the thermal treatment] occurs in the form of annealing of the band in a continual annealing furnace before or after the coating and

wherein the annealing step occurs at a temperature of more than 911°C and, therefore, at any rate above the limit temperature of the two-phase range ferrite/austenite ( $\alpha/\gamma$  range in the iron-carbon system) to austenite range ( $\gamma$  range in the iron-carbon system).

2. (amended) The [A] method according to claim 1, wherein [characterized in that] the coating step [of the band] occurs before the annealing step.

3. (amended) The [A] method according to claim 1, wherein a [characterized in that the] first coating step [of the band] occurs before the annealing step, and that, after the annealing, a second [another] coating is deposited on the band [, preferably through electroplating, that contains the elements of nickel / cobalt / iron / bismuth / indium / palladium / gold or their alloys].

4. (amended) The [A] method of claim 1, wherein [according to one of claims 1 to 3 characterized in that], after the annealing, an additional coating of the band occurs using organic ingredients to enhance [enhancing] the brittleness of the coating [, where the decomposition products of these organic substances, which are a part of the electrolyte bath, and/or reaction products of organic substances, which are a part of the electrolyte bath, are introduced into the coating].

5. (amended) The [A] method of claim 4, wherein [according to claim 4 characterized in that] the organic ingredients [of the electrolyte bath, whose decomposition products and/or reaction products resulting from reactions of these decomposition products with other constituents are introduced into the coating,] are brighteners [(the so-called primary or secondary brighteners)].

6. (amended) The [A] method of claim 1, wherein [according to one of claims 1 to 3 characterized in that] conductive particles [consisting, for example, of carbon, carbon black, graphite, TaS<sub>2</sub>, TiS<sub>2</sub> and/or MoSi<sub>2</sub> ] are embedded into the coating.

7. (amended) The [A] method of claim 1, wherein [according to one of claims 1 to 3 characterized in that] the coating is covered with a dispersion-hardened coating containing conductive particles [such as carbon, carbon black, graphite, TaS<sub>2</sub>, TiS<sub>2</sub> and/or MoSi<sub>2</sub> ].

8. (amended) A cold [Cold] band, preferably for the production of cylindrical containers and especially battery containers by drawing and ironing, said band having two surfaces and comprising [consisting of]:

a band rolled under a cold-rolling ratio of 30 to 95% [,] ;

said band having [with] a carbon content of less than 0.5 weight percent ;

said band further having [as well as with] a coating applied [, preferably in a galvanic process,] to at least one of the two surfaces [of the band, where the coating contains the elements of nickel / cobalt / iron / bismuth / indium / palladium / gold or their alloys],

wherein [characterized in that] the band is a thermally treated band annealed in a continually annealing furnace at a temperature of more than 911°C and, therefore, at any rate above the limit temperature of the two-phase range ferrite / austenite ( $\alpha/\gamma$  range) to austenite range ( $\gamma$  range).

9. (amended) The cold [Cold] band of claim 8, wherein [according to claim 8 characterized in that] the band comprises, over the aforementioned coating, at least one more coating [consisting of the elements of nickel / cobalt / iron / bismuth / indium / palladium / gold or their alloys].

10. (amended) The cold [Cold] band of claim 8, wherein [according to one of claims 8 and 9 characterized in that] conductive particles [consisting, for example, of carbon, carbon black, graphite, TaS<sub>2</sub>, TiS<sub>2</sub> and/or MoSi<sub>2</sub> ] are embedded into the coating.

11. (amended) The cold [Cold] band of claim 8, wherein [according to one of claims 8 and 9 characterized in that] the coating is covered with a dispersion-hardened coating

containing conductive particles [such as carbon, carbon black, graphite, TaS<sub>2</sub>, TiS<sub>2</sub> and/or MoSi<sub>2</sub> ].

12. (amended) The cold [Cold] band of claim 8, wherein:  
carbon is present at no more than 0.3 weight %;  
manganese is present in at least 0.1 weight %;  
manganese is present at no more than 2 weight %;  
silicon is present at no more than 1.0 weight %;  
phosphorus is present at no more than 0.25 weight %;  
sulfur is present at no more than 0.06 weight %;  
aluminum is present in at least 0.015 weight %;  
nitrogen is present at no more than 0.01 weight %; and  
the balance of the material is iron  
[according to one of claims 8 to 11 characterized by the following composition  
(besides iron) (in weight percent):

C max. 0.3 %  
Mn 0.1 to 2 %  
Si max. 1.0 %  
P max. 0.25 %  
S max. 0.06 %  
Al min. 0.015 %  
N max. 0.01 %]

13. (amended) A battery shell characterized in that it is manufactured from the [a] cold band of claim 8 [according to one of claims 8 to 12] by a forming process [, especially by drawing and ironing].

14. (new) The battery shell of claim 13, wherein the forming process is drawing and ironing.

15. (new) The method of claim 1, wherein the coating step is a galvanic process.

16. (new) The method of claim 15, wherein the coating contains nickel.

17. (new) The method of claim 15 wherein the coating contains cobalt.

18. (new) The method of claim 15 wherein the coating contains iron.

19. (new) The method of claim 15 wherein the coating contains bismuth.

20. (new) The method of claim 15 wherein the coating contains indium.

21. (new) The method of claim 15 wherein the coating contains palladium.

22. (new) The method of claim 15 wherein the coating contains gold.

23. (new) The method of claim 15 wherein the coating contains at least two elements selected from the group consisting of: nickel, cobalt, iron, bismuth, indium, palladium, and gold.

24. (new) The method of claim 3, wherein the second coating step is made by electroplating.

25. (new) The method of claim 24, wherein the coating comprises nickel.

26. (new) The method of claim 24 wherein the coating comprises cobalt.

27. (new) The method of claim 24 wherein the coating comprises iron.

28. (new) The method of claim 24 wherein the coating comprises bismuth.

29. (new) The method of claim 24 wherein the coating comprises indium.

30. (new) The method of claim 24 wherein the coating comprises palladium.

31. (new) The method of claim 24 wherein the coating comprises gold.

32. (new) The method of claim 24 wherein the coating comprises at least two elements selected from the group consisting of: nickel, cobalt, iron, bismuth, indium, palladium, and gold.

33. (new) The method of claim 4, wherein the organic ingredients introduced into the coating are the decomposition products of organic substances in the electrolyte bath.

34. (new) The method of claim 4, wherein the organic ingredients introduced into the coating are the reaction products of organic substances in the electrolyte bath.

35. (new) The method of claim 3, wherein, after the annealing, an additional coating of the band occurs using organic ingredients to enhance the brittleness of the coating.

36. (new) The method of claim 35, wherein the organic ingredients introduced into the coating are the decomposition products of organic substances in the electrolyte bath.

37. (new) The method of claim 35, wherein the organic ingredients introduced into the coating are the reaction products of organic substances in the electrolyte bath.

38. (new) The method of claim 35, wherein the organic ingredients are brighteners.

39. (new) The method of claim 6, wherein the conductive particles comprise carbon.

40. (new) The method of claim 6, wherein the conductive particles comprise carbon black.

41. (new) The method of claim 6, wherein the conductive particles comprise graphite.

42. (new) The method of claim 6, wherein the conductive particles comprise  $TaS_2$ .

43. (new) The method of claim 6, wherein the conductive particles comprise  $TiS_2$ .

44. (new) The method of claim 6, wherein the conductive particles comprise  $MoSi_2$ .

45. (new) The method of claim 7, wherein the conductive particles comprise carbon..

46. (new) The method of claim 7, wherein the conductive particles comprise carbon black.

47. (new) The method of claim 7, wherein the conductive particles comprise graphite.

48. (new) The method of claim 7, wherein the conductive particles comprise  $TaS_2$ .

49. (new) The method of claim 7, wherein the conductive particles comprise  $TiS_2$ .

50. (new) The method of claim 7, wherein the conductive particles comprise  $MoSi_2$ .

51. (new) The cold band of claim 8, wherein the coating is applied by a galvanic process.

52. (new) The cold band of claim 51, wherein the coating comprises nickel.

53. (new) The cold band of claim 51 wherein the coating comprises cobalt.

54. (new) The cold band of claim 51 wherein the coating comprises iron.

55. (new) The cold band of claim 51 wherein the coating comprises bismuth.

56. (new) The cold band of claim 51 wherein the coating comprises indium.

57. (new) The cold band of claim 51 wherein the coating comprises palladium.

58. (new) The cold band of claim 51 wherein the coating comprises gold.

59. (new) The cold band of claim 51 wherein the coating comprises at least two elements selected from the group consisting of: nickel, cobalt, iron, bismuth, indium, palladium, and gold.

60. (new) The cold band of claim 9, wherein the additional coating comprises nickel.

61. (new) The cold band of claim 9, wherein the additional coating comprises cobalt.
62. (new) The cold band of claim 9, wherein the additional coating comprises iron.
63. (new) The cold band of claim 9, wherein the additional coating comprises bismuth.
64. (new) The cold band of claim 9, wherein the additional coating comprises indium.
65. (new) The cold band of claim 9, wherein the additional coating comprises palladium.
66. (new) The cold band of claim 9, wherein the additional coating comprises gold.
67. (new) The cold band of claim 9, wherein the additional coating comprises at least two elements selected from the group consisting of: nickel, cobalt, iron, bismuth, indium, palladium, and gold.
68. (new) The cold band of claim 10, wherein the conductive particles comprise carbon.
69. (new) The cold band of claim 10, wherein the conductive particles comprise carbon black.
70. (new) The cold band of claim 10, wherein the conductive particles comprise graphite.
71. (new) The cold band of claim 10, wherein the conductive particles comprise  $TaS_2$ .
72. (new) The cold band of claim 10, wherein the conductive particles comprise  $TiS_2$ .
73. (new) The cold band of claim 10, wherein the conductive particles comprise  $MoSi_2$ .
74. (new) The cold band of claim 11, wherein the conductive particles comprise carbon.
75. (new) The cold band of claim 11, wherein the conductive particles comprise carbon black.

76. (new) The cold band of claim 11, wherein the conductive particles comprise graphite.
77. (new) The cold band of claim 11, wherein the conductive particles comprise  $TaS_2$ .
78. (new) The cold band of claim 11, wherein the conductive particles comprise  $TiS_2$ .
79. (new) The cold band of claim 11, wherein the conductive particles comprise  $MoSi_2$ .

## REMARKS

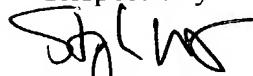
In the specification, paragraph numbers and headings have been introduced, to comply the specification with standard US practice and to facilitate future amendment.

In the claims, multiple dependencies have been removed by distributing the limitations.

The above claims have also been amended to correspond them more closely to United States claiming practice, namely, by removing reference numerals, and by clarifying antecedent basis issues. In this manner, they should be in condition for allowance. These amendments to the claims are fully supported by the literal translation into English of the specification as filed in Germany, and they do not introduce new subject matter.

The claims as amended are incorporated into the substitute specification which is attached hereto.

Respectfully submitted,



Stephen L. Grant  
Reg. No. 33,390  
Hahn Loeser & Parks LLP  
1225 W. Market St.  
Akron, OH 44313  
330-864-5550  
Fax 330-864-7986  
Email: [slgrant@hahnlaw.com](mailto:slgrant@hahnlaw.com)  
Customer No. 021324

**METHOD FOR PRODUCING IMPROVED COLD-ROLLED BAND THAT IS  
CAPABLE OF BEING DEEP-DRAWN OR IRONED, AND COLD-ROLLED BAND,  
PREFERABLY USED FOR PRODUCING CYLINDRICAL CONTAINERS AND, IN  
PARTICULAR, BATTERY CONTAINERS.**

**[0001]** The invention relates to a method for producing improved cold-rolled band that is capable of being deep-drawn or ironed and that has a carbon content of less than 0.5 weight %, during which method the band cold-rolled with a cold-rolling ratio ranging from 30 to 95% is subjected to a thermal treatment in an annealing furnace and to a - preferably galvanic – coating of at least one of the two band surfaces. Furthermore, the invention relates to a cold band, used preferably for producing cylindrical containers and especially battery containers by deep-drawing or ironing, consisting of a band cold-rolled with a cold-rolling ratio ranging from 30 to 95%, with a carbon content of less than 0.5 weight %, and a coating produced in a galvanic process on at least one of the two band surfaces. Finally, the invention relates to a battery shell manufactured from such a cold band.

**Background of the Art**

**[0002]** Document EP 0 809 307 A2 discloses a cold band with coating layers of nickel or nickel alloys deposited in a galvanic process. A part of the procedure is, furthermore, an annealing process performed in a multiple sequence, during which the steel band with a nickel coating is first annealed at the temperature of 640° C, i.e., the recrystallization temperature of the steel, with a subsequent annealing process at the same temperature, before another thermal treatment at a furnace temperature of 450° C finally occurs. A consequence of the sequentially performed annealing processes is a change in the arrangement and nature of the structural crystals. The procedure according to EP 0 809 307 A2 endeavors to accomplish, by selecting corresponding galvanization processes, when the band is deep-drawn or ironed into battery shells that the harder of the two band surfaces later forms the inner side of the battery shell, whereas the other side – also coated with a nickel alloy but of lesser hardness – later forms the outer side of the battery.

**[0003]** Document DE 37 26 518 C2 describes a procedure for producing nickel-plated and cobalt-plated cold band that is subjected to thermal treatment at a temperature in the range of 580° to 710° C. The cold band with a carbon content of up to 0.07 weight % used in

this procedure is pickled, cold-rolled, subsequently nickel-plated in a galvanic process, and then annealed at a temperature in the range of 580° to 710° C to achieve recrystallization. Then follows rerolling or killing of the improved band. The method further proposes to deposit an additional layer of cobalt on the electrolytically applied nickel coating, which has a positive impact on the resistance of the finished band to corrosion. Furthermore, the document points out an enhanced diffusion speed due to the crystallization annealing, where the penetration of the coating metals into the base material of the steel band by way of diffusion demonstrates a depth several times greater than the depth of the nickel-cobalt coating.

**[0004]** Document EP 0 629 009 B1 describes a method for producing of a nickel-plated cold band with very low earing and an especially low carbon content of less than 0.009 weight %. Various alternatives are provided for the performance of the method and the sequence of the individual procedure steps. So, for example, it describes how after the nickel-plating process the annealed steel band is annealed a second time, which, however, results in a costly overall process. Furthermore, the document also describes how the cold band is first annealed and only then subjected to a galvanic process of nickel-plating, without any following diffusion annealing. The temperature range of 600° to 900° C is indicated for the continual annealing process, and 2 minutes are indicated for the duration of annealing.

**[0005]** The task of this invention is to propose a method for producing improved cold-rolled band that is capable of being deep-drawn or ironed with a carbon content of less than 0.5 weight % resulting in an isotropic steel band that has a low level of texturing and that has a low tendency to form earing.

#### **Detailed Description of the Preferred Embodiment**

**[0006]** To resolve this task, the invention proposes a method of the nature described at the beginning, according to which a single or multiple coating contains the elements of nickel / cobalt / iron / bismuth / indium / palladium / gold / tin or their alloys and the thermal treatment occurs in the form of annealing of the band in a continually annealing furnace, before or after the coating, at a temperature above the limit temperature of the two-phase range ferrite / austenite ( $\alpha/\gamma$  range in the iron-carbon system) to austenite range ( $\gamma$  range in the iron-carbon system).

[0007] As a result of the normalization annealing with double crossing of the limit to the  $\gamma$  range, the steel is brought into a fine-grained, homogeneous structure condition. Any structural and property changes caused by the preceding warm and cold forming processes and any thermal treatment are reversed by the normalization annealing above the limit temperature to the austenite range ( $\gamma$  range). What happens is a comprehensive recrystallization of the structure resulting in a relatively small grain, which leads to a very low tendency to form earings, expressed by planar anisotropy  $\Delta r$ , during the subsequent use of the steel band for deep-drawing or ironing, e.g., of battery shells. The achieved small grain of globular shape is suitable even for extreme drawing ratios, where the fine structure causes a smooth surface of the drawn part. In addition, the fine-grain structure achieved by the normalization annealing in a continual annealing furnace enhances the corrosion resistance of the part drawn from improved cold band. The reason is a significantly diminished scale of forming small cracks in the galvanic coating during the drawing or ironing due to the very small grain size of the substrate.

[0008] The homogenizing of the mechanical properties and a complete change in the structural texture throughout the entire length and width of the band connected with the double structure transformation can also result in an increase in strength as compared to recrystallized material. This is advantageous especially for multiple-step drawing and ironing operations, which are performed at a high speed, e.g., in fast running presses. It diminishes the danger of necking and cracking defined by the tensile strength of the material.

[0009] Furthermore, as a result of the increased strength of the galvanized cold band, the normalization annealing in a continual annealing furnace leads to improved dimensional stability and very low earing formation in the drawn part, which is important especially in the manufacturing of battery shells or similar rotationally symmetrical products. The temperature required for the normalization annealing in a continual annealing furnace according to this invention depends on the carbon content in the used band material. For a decarbonized steel with a carbon content of no more than 0.01 weight %, the annealing temperature should lie in the range of 950° to 1000° C with treatment duration of no more than 10 minutes. For higher carbon contents, e.g., 0.3 weight %, the annealing temperature is lower by about 100° C; however, it still lies within the austenite range of the iron-carbon system.

**[0010]** The coating according to this invention is preferably deposited in a galvanic process, however, vacuum metallizing is also possible. Both procedures allow single-layer coating as well as multiple-layer coating. The coating of the two sides of the band can also be different from each other in order to achieve different mechanical, tribological and/or electrical properties on the two sides to improve the deep-drawing process.

**[0011]** If the coating, as proposed by this invention, containing the elements of nickel / cobalt / iron / bismuth / indium / palladium / gold / tin or their alloys is deposited before the annealing process, the coating adheres to the band material especially well due to diffusion [of the elements] deep into the material of the steel band caused by the thermal treatment. During the subsequent deep-drawing and ironing, a separation of the deposited coating layers from the base material becomes impossible. The normalization annealing at a temperature in the austenite range causes that the coating deposited on the band material and having an amorphous deposition structure is transformed into a globular structure with an improved ductility.

**[0012]** In order to achieve diffusion of the coating into the base material of the steel band of a sufficient penetration depth, the coating must occur before the annealing process. Another design version of the method proposes that the first coating is applied before the annealing process, and a second coating containing the elements of nickel / cobalt / iron / bismuth / indium / palladium / gold / tin or their alloys is deposited on the band after the annealing process.

**[0013]** To further improve the band's behavior during the deep drawing, after the normalization annealing the band should first be subjected to a temper pass roll procedure.

**[0014]** The additional coating process following the annealing process and the rerolling procedure should be performed using a galvanic bath with added organic ingredients in order to increase the hardness and brittleness of the resulting coating. This causes - at a later stage, during the drawing or ironing of the shell manufactured from the cold band according to this invention - the very brittle coating to crack open. If subjected to strong forming forces during the deep drawing or ironing, the side bearing a coating demonstrates an especially low electrical contact resistance, which is especially advantageous in the

manufacturing of batteries with alkaline electrolytes. In comparison with the current state of art, the inner side of a battery shell manufactured in such a manner demonstrates very low values of the electrical contact resistance between the cathode substance of the battery and the inner surface of the battery shell.

**[0015]** The addition of the aforementioned organic ingredients to the electrolyte bath is especially advantageous if the subsequent coating is made of cobalt or a cobalt alloy.

**[0016]** Furthermore, it is advantageous to additionally introduce electrically conductive particles into the layer containing organic ingredients in order to improve its conductivity.

**[0017]** Electrically conductive particles of such substances as carbon, carbon black, graphite,  $TaS_2$ ,  $TiS_2$  and/or  $MoSi_2$  can also be introduced into the first coating deposited before the annealing process. When the cold band is later used to manufacture battery shells, the contact resistance of the shell can be diminished using such imbedded particles. In addition, it is possible to deposit – in a galvanic process - a dispersion layer containing conductive particles such as carbon, carbon black, graphite,  $TaS_2$ ,  $TiS_2$  and/or  $MoSi_2$  on top of the previous coating. The carbon content in the galvanic layer should be between 0.7 and 15 weight %. The most convenient material for the carbon suspended in the galvanic bath are finely distributed particles of carbon (graphite or carbon black). The particle size is preferably between 0.5 to 15  $\mu m$ .

**[0018]** During the galvanization process a steady flow should be maintained in the galvanic bath in order to achieve a uniform distribution of the carbon in the galvanic layer. In order to achieve the steady flow, the galvanic bath is preferably revolved at a steady pace. A forced electrolyte flow speed of 6 to 10 m/s proved to be especially suitable. Furthermore, the galvanic bath can contain suspension-stabilizing and/or anti-clotting substances, in order to achieve a uniform distribution of the particles of carbon without any local or temporary concentrations.

**[0019]** In order to resolve the aforementioned task, this invention proposes with regard to the cold band with the initially indicated characteristics, that the coating contain the

elements of nickel / cobalt / iron / bismuth / indium / palladium / gold / tin or their alloys, and that the band be thermally treated in a continual annealing furnace at an annealing temperature above the limit temperature of the two-phase range ferrite / austenite ( $\alpha/\gamma$  range) to austenite range ( $\gamma$  range).

**[0020]** Finally, the invention proposes that, besides the first coating, the cold band comprise an additional layer of the elements of nickel / cobalt / iron / bismuth / indium / palladium / gold / tin or their alloys. The following metals and their combinations are most convenient for the layer to be deposited in a galvanic or vacuum metallizing process: Cobalt, nickel/iron, nickel/cobalt, nickel/cobalt/iron, cobalt/iron, nickel/indium, iron/indium, nickel/bismuth, palladium, palladium/nickel, palladium/iron, palladium/cobalt, palladium/indium, and palladium/bismuth.

**[0021]** The temperature in a continual annealing furnace required for the normalization annealing of the cold band according to this invention depends on the carbon content in the band material used. For the so-called decarbonized steel with a carbon content of no more than 0.01 weight %, the annealing temperature should lie in the range of 950° to 1000°C with treatment duration of no more than 10 minutes. For higher carbon contents, e.g., 0.3 weight %, the annealing temperature is lower by about 100° C; however, it still lies within the austenite range of the iron-carbon system.

**[0022]** Subsequent to the normalization annealing process, an additional coating, preferably of cobalt or a cobalt alloy, can be deposited in a galvanic process. Organic ingredients are added to the electrolyte bath. Due to the flow of electrolyte during the galvanic coating process, the organic ingredients disintegrate into decomposition products. These products can then react with other substances contained in the electrolyte bath, e.g., with metal ions. Such reaction products are deposited, together with other decomposition products and cobalt or a cobalt alloy, on the cold band, and cause that the layer becomes significantly more brittle. In case of organic substances containing sulfur or carbon, these reaction products can be, e.g., cobalt sulfides or cobalt carbides.

**[0023]** The primary and secondary brighteners known from the galvanic nickel-plating process are suitable as organic ingredients of the electrolyte. Galvanic deposits

involving by such ingredients result in a very hard and, at the same time, brittle coating, which is why the material has a strong tendency to crack during the forming process by way of deep drawing or ironing at a later stage. These cracks distinguish themselves by a relatively uniform structure with lozenge-shaped crack slabs.

**[0024]** Suitable brighteners proved to be substances such as 1,4 butindiol, o-benzoic acid sulfimide (saccharine), paratoluolsulfonamide, and mixtures of these substances. The bath with such brighteners and an electrolyte prevailingly containing cobalt should be operated at an electrolyte temperature of 50 to 70°C and a current density of 6 – 15 A/dm<sup>2</sup>. The pH value of the electrolyte bath should preferably be set to 4.0.

**[0025]** The following text indicates, as examples, five different steel compositions suitable, according to the present invention, for the base material of a thickness of 0.1 to 1 mm:

### **1. Unalloyed, carbon-lean steel**

|            |                |
|------------|----------------|
| Carbon     | 0.010 – 0.100% |
| Manganese  | 0.140 – 0.345% |
| Silicon    | max. 0.06%     |
| Phosphorus | max. 0.025%    |
| Sulfur     | max. 0.030%    |
| Aluminum   | 0.02 – 0.08%   |
| Nitrogen   | max. 0.0080%   |
| Copper     | max. 0.10%     |
| Chromium   | max. 0.10%     |
| Nickel     | max. 0.10%     |
| Boron      | max. 0.006%    |
| Titanium   | max. 0.015%    |
| Rest:      | Iron           |

### **2. Decarbonized steel (Interstitial-free steel)**

|            |                |
|------------|----------------|
| Carbon     | max. 0.010%    |
| Manganese  | 0.10 – 0.25%   |
| Silicon    | max. 0.15%     |
| Phosphorus | max. 0.020%    |
| Sulfur     | max. 0.020%    |
| Aluminum   | 0.015 – 0.060% |
| Nitrogen   | max. 0.004%    |
| Copper     | max. 0.08%     |
| Chromium   | max. 0.06%     |
| Nickel     | max. 0.10%     |
| Titanium   | 0.02 – 0.10%   |
| Niobium    | max. 0.10%     |
| Rest:      | Iron           |

### 3. Low-carbon steel

|            |                |
|------------|----------------|
| Carbon     | 0.010 – 0.020% |
| Manganese  | 0.50 – 0.70%   |
| Silicon    | max. 0.06%     |
| Phosphorus | max. 0.025%    |
| Sulfur     | max. 0.020%    |
| Aluminum   | 0.02 – 0.08%   |
| Nitrogen   | max. 0.009%    |
| Copper     | max. 0.12%     |
| Chromium   | max. 0.06%     |
| Nickel     | max. 0.10%     |
| Rest:      | Iron           |

### 4. Micro-alloyed steel

|            |                 |
|------------|-----------------|
| Carbon     | max 0.10%       |
| Manganese  | max. 1.65%      |
| Silicon    | max. 0.50%      |
| Phosphorus | max. 0.12%      |
| Sulfur     | max. 0.030%     |
| Aluminum   | at least 0.015% |
| Niobium    | max. 0.09%      |
| Titanium   | max. 0.22%      |
| Vanadium   | max. 0.25%      |
| Rest:      | Iron            |

## 5. Super high-strength, micro-alloyed steel

|            |             |
|------------|-------------|
| Carbon     | max 0.25%   |
| Manganese  | max. 1.65%  |
| Silicon    | max. 0.60%  |
| Aluminum   | min. 0.02%  |
| Phosphorus | max. 0.025% |
| Sulfur     | max. 0.035% |
| Vanadium   | min. 0.03%  |
| Niobium    | min. 0.03%  |
| Molybdenum | min. 0.20%  |

Rest: Iron

(The percentage value designate weight percent).

## Claims

What is claimed is:

1. (amended) A method for producing improved cold band suitable for drawing or ironing process, with a carbon content of less than 0.5 weight percent, said cold band having two surfaces, the method comprising the steps of:
  - rolling the cold band under a cold-rolling ratio of at least 30% and less than 95%;
  - annealing the cold band by a thermal treatment in an annealing furnace; and
  - coating the cold band, preferably on a galvanic basis, on at least one of the surfaces, wherein the annealing step occurs in the form of annealing of the band in a continual annealing furnace before or after the coating andwherein the annealing step occurs at a temperature of more than 911°C and, therefore, at any rate above the limit temperature of the two-phase range ferrite/austenite ( $\alpha/\gamma$  range in the iron-carbon system) to austenite range ( $\gamma$  range in the iron-carbon system).
2. (amended) The method according to claim 1, wherein the coating step occurs before the annealing step.
3. (amended) The method according to claim 1, wherein a first coating step occurs before the annealing step, and that, after the annealing, a second coating is deposited on the band.
4. (amended) The method of claim 1, wherein, after the annealing, an additional coating of the band occurs using organic ingredients to enhance the brittleness of the coating.
5. (amended) The method of claim 4, wherein the organic ingredients are brighteners.
6. (amended) The method of claim 1, wherein conductive particles are embedded into the coating.

7. (amended) The method of claim 1, wherein the coating is covered with a dispersion-hardened coating containing conductive particles.

8. (amended) A cold band, preferably for the production of cylindrical containers and especially battery containers by drawing and ironing, said band having two surfaces and comprising:

a band rolled under a cold-rolling ratio of 30 to 95%;

said band having a carbon content of less than 0.5 weight percent;

said band further having a coating applied;

wherein the band is a thermally treated band annealed in a continually annealing furnace at a temperature of more than 911°C and, therefore, at any rate above the limit temperature of the two-phase range ferrite / austenite ( $\alpha/\gamma$  range) to austenite range ( $\gamma$  range).

9. (amended) The cold band of claim 8, wherein the band comprises, over the aforementioned coating, at least one more coating.

10. (amended) The cold band of claim 8, wherein conductive particles are embedded into the coating.

11. (amended) The cold band of claim 8, wherein the coating is covered with a dispersion-hardened coating containing conductive particles.

12. (amended) The cold band of claim 8, wherein:

carbon is present at no more than 0.3 weight %;

manganese is present in at least 0.1 weight %;

manganese is present at no more than 2 weight %;

silicon is present at no more than 1.0 weight %;

phosphorus is present at no more than 0.25 weight %;

sulfur is present at no more than 0.06 weight %;

aluminum is present in at least 0.015 weight %;

nitrogen is present at no more than 0.01 weight %; and

the balance of the material is iron.

13. (amended) A battery shell characterized in that it is manufactured from the cold band of claim 8 by a forming process.

14. (new) The battery shell of claim 13, wherein the forming process is drawing and ironing.

15. (new) The method of claim 1, wherein the coating step is a galvanic process.

16. (new) The method of claim 15, wherein the coating contains nickel.

17. (new) The method of claim 15 wherein the coating contains cobalt.

18. (new) The method of claim 15 wherein the coating contains iron.

19. (new) The method of claim 15 wherein the coating contains bismuth.

20. (new) The method of claim 15 wherein the coating contains indium.

21. (new) The method of claim 15 wherein the coating contains palladium.

22. (new) The method of claim 15 wherein the coating contains gold.

23. (new) The method of claim 15 wherein the coating contains at least two elements selected from the group consisting of: nickel, cobalt, iron, bismuth, indium, palladium, and gold.

24. (new) The method of claim 3, wherein the second coating step is made by electroplating.

25. (new) The method of claim 24, wherein the coating comprises nickel.

26. (new) The method of claim 24 wherein the coating comprises cobalt.

27. (new) The method of claim 24 wherein the coating comprises iron.

28. (new) The method of claim 24 wherein the coating comprises bismuth.

29. (new) The method of claim 24 wherein the coating comprises indium.

30. (new) The method of claim 24 wherein the coating comprises palladium.

31. (new) The method of claim 24 wherein the coating comprises gold.

32. (new) The method of claim 24 wherein the coating comprises at least two elements selected from the group consisting of: nickel, cobalt, iron, bismuth, indium, palladium, and gold.

33. (new) The method of claim 4, wherein the organic ingredients introduced into the coating are the decomposition products of organic substances in the electrolyte bath.

34. (new) The method of claim 4, wherein the organic ingredients introduced into the coating are the reaction products of organic substances in the electrolyte bath.

35. (new) The method of claim 3, wherein, after the annealing, an additional coating of the band occurs using organic ingredients to enhance the brittleness of the coating.

36. (new) The method of claim 35, wherein the organic ingredients introduced into the coating are the decomposition products of organic substances in the electrolyte bath.

37. (new) The method of claim 35, wherein the organic ingredients introduced into the coating are the reaction products of organic substances in the electrolyte bath.

38. (new) The method of claim 35, wherein the organic ingredients are brighteners.

39. (new) The method of claim 6, wherein the conductive particles comprise carbon.

40. (new) The method of claim 6, wherein the conductive particles comprise carbon black.

41. (new) The method of claim 6, wherein the conductive particles comprise graphite.

42. (new) The method of claim 6, wherein the conductive particles comprise  $TaS_2$ .

43. (new) The method of claim 6, wherein the conductive particles comprise  $TiS_2$

44. (new) The method of claim 6, wherein the conductive particles comprise  $MoSi_2$ .

45. (new) The method of claim 7, wherein the conductive particles comprise carbon..

46. (new) The method of claim 7, wherein the conductive particles comprise carbon black.

47. (new) The method of claim 7, wherein the conductive particles comprise graphite.

48. (new) The method of claim 7, wherein the conductive particles comprise  $TaS_2$ .

49. (new) The method of claim 7, wherein the conductive particles comprise  $TiS_2$ .

50. (new) The method of claim 7, wherein the conductive particles comprise  $MoSi_2$ .

51. (new) The cold band of claim 8, wherein the coating is applied by a galvanic process.

52. (new) The cold band of claim 51, wherein the coating comprises nickel.

53. (new) The cold band of claim 51 wherein the coating comprises cobalt.

54. (new) The cold band of claim 51 wherein the coating comprises iron.

55. (new) The cold band of claim 51 wherein the coating comprises bismuth.

56. (new) The cold band of claim 51 wherein the coating comprises indium.

57. (new) The cold band of claim 51 wherein the coating comprises palladium.

58. (new) The cold band of claim 51 wherein the coating comprises gold.

59. (new) The cold band of claim 51 wherein the coating comprises at least two elements selected from the group consisting of: nickel, cobalt, iron, bismuth, indium, palladium, and gold.

60. (new) The cold band of claim 9, wherein the additional coating comprises nickel.

61. (new) The cold band of claim 9, wherein the additional coating comprises cobalt.

62. (new) The cold band of claim 9, wherein the additional coating comprises iron.

63. (new) The cold band of claim 9, wherein the additional coating comprises bismuth.

64. (new) The cold band of claim 9, wherein the additional coating comprises indium.

65. (new) The cold band of claim 9, wherein the additional coating comprises palladium.

66. (new) The cold band of claim 9, wherein the additional coating comprises gold.

67. (new) The cold band of claim 9, wherein the additional coating comprises at least two elements selected from the group consisting of: nickel, cobalt, iron, bismuth, indium, palladium, and gold.

68. (new) The cold band of claim 10, wherein the conductive particles comprise carbon.

69. (new) The cold band of claim 10, wherein the conductive particles comprise carbon black.

70. (new) The cold band of claim 10, wherein the conductive particles comprise graphite.

71. (new) The cold band of claim 10, wherein the conductive particles comprise  $TaS_2$ .

72. (new) The cold band of claim 10, wherein the conductive particles comprise  $TiS_2$ .

73. (new) The cold band of claim 10, wherein the conductive particles comprise  $MoSi_2$ .

74. (new) The cold band of claim 11, wherein the conductive particles comprise carbon.

75. (new) The cold band of claim 11, wherein the conductive particles comprise carbon black.

76. (new) The cold band of claim 11, wherein the conductive particles comprise graphite.

77. (new) The cold band of claim 11, wherein the conductive particles comprise  $TaS_2$ .

78. (new) The cold band of claim 11, wherein the conductive particles comprise  $TiS_2$ .

79. (new) The cold band of claim 11, wherein the conductive particles comprise  $MoSi_2$ .

(12) International application published according to the International Patent Cooperation Treaty

(19) **World Intellectual Property Organization  
International Office**

(43) **International Publication Date:** 15 February 2001 (2/15/2001)

(10) **International Publication Number:** WO 01/11114 A1

(51) **International Patent Classification:** C25D 5/50

(21) **International Reference:** PCT/EP00/07503

(22) **International Application Date:** 3 August 2000 (8/3/2000)

(25) **Language of Submission:** German

(26) **Language of Publication:** German

(30) **Information about Priority:** 199 37 271.3 6 August 1999 (8/6/1999) DE

(71) **Applicant (for all countries of destination except for the USA):** HILLE & MÜLLER GMBH & CO. [DE/DE]; Am Trippelsberg 48, 40589 Düsseldorf (DE).

(72) **Inventor; and**

(75) **Inventor/Applicant (only for the USA):** PFEIFENBRING, Karlfried [DE/DE]; Swakopmunder Strasse 18b, 47249 Duisburg (DE). STEINMANN, Hans-Günter [DE/DE]; Otto-Hahn-Strasse 18, 40591 Düsseldorf (DE). SCHMIDT, Ferdinand [DE/DE]; Kammerathsfeldstrasse 56, Düsseldorf (DE). OLBERDING, Werner [DE/DE]; Am Feldgen 32, 42553 Velbert (DE). RUBART, Marcel, Sébastien [DE/DE]; Am Stadtbad 56, 46537 Dinslaken (DE).

(74) **Attorney:** STENGER, WATZKE & RING; Kaiser-Friedrich-Ring 70, 40547 Düsseldorf (DE).

(81) **Countries of Destination (National):** AU, BR, CA, CN, IL, IN, JP, KR, MX, PL, RU, SG, US.

(84) **Countries of Destination (Regional):** European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).

**Published:**

- With international search report
- Before the expiration of the period set for a modification of the claims; the publication is to be repeated if modifications are performed.

Regarding the two-letter codes and other abbreviations we wish to refer to the guidance notes on codes and abbreviations at the beginning of each regular issue of the PCT Gazette.

(54) **Title:** Method for producing improved cold-rolled band that is capable of being deep-drawn or ironed, and cold-rolled band, preferably used for producing cylindrical containers and, in particular, battery containers

(57) **Abstract:** The invention relates to a method for producing improved cold-rolled band that is capable of being deep-drawn or ironed and that has a carbon content of less than 0.5 weight %. The invention also relates to a cold-rolled band that can be produced by such a method, and preferably used for producing cylindrical containers and, in particular, battery containers by deep-drawing or ironing. The band that is cold-rolled with a cold-rolling ratio ranging from 30 to 95% is subjected to a thermal treatment in an annealing furnace and to a - preferably galvanic – coating of at least one of the two band surfaces. In order to obtain an isotropic steel band that has a low level of texturing and that has a low tendency to form earing, the coating produced with one or multiple layers contains the elements of nickel / cobalt / iron / bismuth / indium / palladium / gold / tin, or alloys thereof, where the thermal treatment is effected by annealing, which is carried out - before or after the coating process – in a continuously running band-annealing furnace at a temperature greater than the limit temperature of the austenite range ( $\gamma$  range).

**Method for producing improved cold-rolled band that is capable of being deep-drawn or ironed, and cold-rolled band, preferably used for producing cylindrical containers and, in particular, battery containers.**

The invention relates to a method for producing improved cold-rolled band that is capable of being deep-drawn or ironed and that has a carbon content of less than 0.5 weight %, during which method the band cold-rolled with a cold-rolling ratio ranging from 30 to 95% is subjected to a thermal treatment in an annealing furnace and to a - preferably galvanic – coating of at least one of the two band surfaces. Furthermore, the invention relates to a cold band, used preferably for producing cylindrical containers and especially battery containers by deep-drawing or ironing, consisting of a band cold-rolled with a cold-rolling ratio ranging from 30 to 95%, with a carbon content of less than 0.5 weight %, and a coating produced in a galvanic process on at least one of the two band surfaces. Finally, the invention relates to a battery shell manufactured from such a cold band.

Document EP 0 809 307 A2 discloses a cold band with coating layers of nickel or nickel alloys deposited in a galvanic process. A part of the procedure is, furthermore, an annealing process performed in a multiple sequence, during which the steel band with a nickel coating is first annealed at the temperature of 640° C, i.e., the recrystallization temperature of the steel, with a subsequent annealing process at the same temperature, before another thermal treatment at a furnace temperature of 450° C finally occurs. A consequence of the sequentially performed annealing processes is a change in the arrangement and nature of the structural crystals. The procedure according to EP 0 809 307 A2 endeavors to accomplish, by selecting corresponding galvanization processes, when the band is deep-drawn or ironed into battery shells that the harder of the two band surfaces later forms the inner side of the battery shell, whereas the other side – also coated with a nickel alloy but of lesser hardness – later forms the outer side of the battery.

Document DE 37 26 518 C2 describes a procedure for producing nickel-plated and cobalt-plated cold band that is subjected to thermal treatment at a temperature in the range of 580° to 710° C. The cold band with a carbon content of up to 0.07 weight % used in this procedure is pickled, cold-rolled, subsequently nickel-plated in a galvanic process, and then annealed at a temperature in the range of 580° to 710° C to achieve recrystallization. Then follows rerolling or killing of the improved band. The method further proposes to deposit an additional layer of cobalt on the electrolytically applied nickel coating, which has a positive impact on the resistance of the finished band to corrosion. Furthermore, the document points out an enhanced diffusion speed due to the crystallization annealing, where the penetration of the coating metals into the base material of the steel band by way of diffusion demonstrates a depth several times greater than the depth of the nickel-cobalt coating.

Document EP 0 629 009 B1 describes a method for producing of a nickel-plated cold band with very low earing and an especially low carbon content of less than 0.009 weight %. Various alternatives are provided for the performance of the method and the sequence of the individual procedure steps. So, for example, it describes how after the nickel-plating process the annealed

steel band is annealed a second time, which, however, results in a costly overall process. Furthermore, the document also describes how the cold band is first annealed and only then subjected to a galvanic process of nickel-plating, without any following diffusion annealing. The temperature range of 600° to 900° C is indicated for the continual annealing process, and 2 minutes are indicated for the duration of annealing.

The task of this invention is to propose a method for producing improved cold-rolled band that is capable of being deep-drawn or ironed with a carbon content of less than 0.5 weight % resulting in an isotropic steel band that has a low level of texturing and that has a low tendency to form earing.

To resolve this task, the invention proposes a method of the nature described at the beginning, according to which a single or multiple coating contains the elements of nickel / cobalt / iron / bismuth / indium / palladium / gold / tin or their alloys and the thermal treatment occurs in the form of annealing of the band in a continually annealing furnace, before or after the coating, at a temperature above the limit temperature of the two-phase range ferrite / austenite ( $\alpha/\gamma$  range in the iron-carbon system) to austenite range ( $\gamma$  range in the iron-carbon system).

As a result of the normalization annealing with double crossing of the limit to the  $\gamma$  range, the steel is brought into a fine-grained, homogeneous structure condition. Any structural and property changes caused by the preceding warm and cold forming processes and any thermal treatment are reversed by the normalization annealing above the limit temperature to the austenite range ( $\gamma$  range). What happens is a comprehensive recrystallization of the structure resulting in a relatively small grain, which leads to a very low tendency to form earings, expressed by planar anisotropy  $\Delta r$ , during the subsequent use of the steel band for deep-drawing or ironing, e.g., of battery shells. The achieved small grain of globular shape is suitable even for extreme drawing ratios, where the fine structure causes a smooth surface of the drawn part. In addition, the fine-grain structure achieved by the normalization annealing in a continual annealing furnace enhances the corrosion resistance of the part drawn from improved cold band. The reason is a significantly diminished scale of forming small cracks in the galvanic coating during the drawing or ironing due to the very small grain size of the substrate.

The homogenizing of the mechanical properties and a complete change in the structural texture throughout the entire length and width of the band connected with the double structure transformation can also result in an increase in strength as compared to recrystallized material. This is advantageous especially for multiple-step drawing and ironing operations, which are performed at a high speed, e.g., in fast running presses. It diminishes the danger of necking and cracking defined by the tensile strength of the material.

Furthermore, as a result of the increased strength of the galvanized cold band, the normalization annealing in a continual annealing furnace leads to improved dimensional stability and very low earing formation in the drawn part, which is important especially in the manufacturing of battery shells or similar rotationally symmetrical products. The temperature required for the normalization annealing in a continual annealing furnace according to this invention depends on the carbon content in the used band material. For a decarbonized steel with a carbon content of no more than 0.01 weight %, the annealing temperature should lie in the range of 950° to 1000° C with treatment duration of no more than 10 minutes. For higher carbon contents, e.g., 0.3

weight %, the annealing temperature is lower by about 100° C; however, it still lies within the austenite range of the iron-carbon system.

The coating according to this invention is preferably deposited in a galvanic process, however, vacuum metallizing is also possible. Both procedures allow single-layer coating as well as multiple-layer coating. The coating of the two sides of the band can also be different from each other in order to achieve different mechanical, tribological and/or electrical properties on the two sides to improve the deep-drawing process.

If the coating, as proposed by this invention, containing the elements of nickel / cobalt / iron / bismuth / indium / palladium / gold / tin or their alloys is deposited before the annealing process, the coating adheres to the band material especially well due to diffusion [of the elements] deep into the material of the steel band caused by the thermal treatment. During the subsequent deep-drawing and ironing, a separation of the deposited coating layers from the base material becomes impossible. The normalization annealing at a temperature in the austenite range causes that the coating deposited on the band material and having an amorphous deposition structure is transformed into a globular structure with an improved ductility.

In order to achieve diffusion of the coating into the base material of the steel band of a sufficient penetration depth, the coating must occur before the annealing process. Another design version of the method proposes that the first coating is applied before the annealing process, and a second coating containing the elements of nickel / cobalt / iron / bismuth / indium / palladium / gold / tin or their alloys is deposited on the band after the annealing process.

To further improve the band's behavior during the deep drawing, after the normalization annealing the band should first be subjected to a temper pass roll procedure.

The additional coating process following the annealing process and the rerolling procedure should be performed using a galvanic bath with added organic ingredients in order to increase the hardness and brittleness of the resulting coating. This causes - at a later stage, during the drawing or ironing of the shell manufactured from the cold band according to this invention - the very brittle coating to crack open. If subjected to strong forming forces during the deep drawing or ironing, the side bearing a coating demonstrates an especially low electrical contact resistance, which is especially advantageous in the manufacturing of batteries with alkaline electrolytes. In comparison with the current state of art, the inner side of a battery shell manufactured in such a manner demonstrates very low values of the electrical contact resistance between the cathode substance of the battery and the inner surface of the battery shell.

The addition of the aforementioned organic ingredients to the electrolyte bath is especially advantageous if the subsequent coating is made of cobalt or a cobalt alloy.

Furthermore, it is advantageous to additionally introduce electrically conductive particles into the layer containing organic ingredients in order to improve its conductivity.

Electrically conductive particles of such substances as carbon, carbon black, graphite,  $TaS_2$ ,  $TiS_2$  and/or  $MoSi_2$  can also be introduced into the first coating deposited before the annealing process. When the cold band is later used to manufacture battery shells, the contact resistance of the shell can be diminished using such imbedded particles. In addition, it is possible to deposit – in a

galvanic process - a dispersion layer containing conductive particles such as carbon, carbon black, graphite,  $TaS_2$ ,  $TiS_2$  and/or  $MoSi_2$  on top of the previous coating. The carbon content in the galvanic layer should be between 0.7 and 15 weight %. The most convenient material for the carbon suspended in the galvanic bath are finely distributed particles of carbon (graphite or carbon black). The particle size is preferably between 0.5 to 15  $\mu m$ .

During the galvanization process a steady flow should be maintained in the galvanic bath in order to achieve a uniform distribution of the carbon in the galvanic layer. In order to achieve the steady flow, the galvanic bath is preferably revolved at a steady pace. A forced electrolyte flow speed of 6 to 10 m/s proved to be especially suitable. Furthermore, the galvanic bath can contain suspension-stabilizing and/or anti-clotting substances, in order to achieve a uniform distribution of the particles of carbon without any local or temporary concentrations.

In order to resolve the aforementioned task, this invention proposes with regard to the cold band with the initially indicated characteristics, that the coating contain the elements of nickel / cobalt / iron / bismuth / indium / palladium / gold / tin or their alloys, and that the band be thermally treated in a continual annealing furnace at an annealing temperature above the limit temperature of the two-phase range ferrite / austenite ( $\alpha/\gamma$  range) to austenite range ( $\gamma$  range).

Finally, the invention proposes that, besides the first coating, the cold band comprise an additional layer of the elements of nickel / cobalt / iron / bismuth / indium / palladium / gold / tin or their alloys. The following metals and their combinations are most convenient for the layer to be deposited in a galvanic or vacuum metallizing process:

Cobalt, nickel/iron, nickel/cobalt, nickel/cobalt/iron, cobalt/iron, nickel/indium, iron/indium, nickel/bismuth, palladium, palladium/nickel, palladium/iron, palladium/cobalt, palladium/indium, and palladium/bismuth.

The temperature in a continual annealing furnace required for the normalization annealing of the cold band according to this invention depends on the carbon content in the band material used. For the so-called decarbonized steel with a carbon content of no more than 0.01 weight %, the annealing temperature should lie in the range of 950° to 1000°C with treatment duration of no more than 10 minutes. For higher carbon contents, e.g., 0.3 weight %, the annealing temperature is lower by about 100° C; however, it still lies within the austenite range of the iron-carbon system.

Subsequent to the normalization annealing process, an additional coating, preferably of cobalt or a cobalt alloy, can be deposited in a galvanic process. Organic ingredients are added to the electrolyte bath. Due to the flow of electrolyte during the galvanic coating process, the organic ingredients disintegrate into decomposition products. These products can then react with other substances contained in the electrolyte bath, e.g., with metal ions. Such reaction products are deposited, together with other decomposition products and cobalt or a cobalt alloy, on the cold band, and cause that the layer becomes significantly more brittle. In case of organic substances containing sulfur or carbon, these reaction products can be, e.g., cobalt sulfides or cobalt carbides.

The primary and secondary brighteners known from the galvanic nickel-plating process are suitable as organic ingredients of the electrolyte. Galvanic deposits involving by such ingredients result in a very hard and, at the same time, brittle coating, which is why the material has a strong tendency to crack during the forming process by way of deep drawing or ironing at a later stage. These cracks distinguish themselves by a relatively uniform structure with lozenge-shaped crack slabs.

Suitable brighteners proved to be substances such as 1,4 butindiol, o-benzoic acid sulfimide (saccharine), paratoluolsulfonamide, and mixtures of these substances. The bath with such brighteners and an electrolyte prevailingly containing cobalt should be operated at an electrolyte temperature of 50 to 70°C and a current density of 6 – 15 A/dm<sup>2</sup>. The pH value of the electrolyte bath should preferably be set to 4.0.

The following text indicates, as examples, five different steel compositions suitable, according to the present invention, for the base material of a thickness of 0.1 to 1 mm:

### **1. Unalloyed, carbon-lean steel**

|            |                |
|------------|----------------|
| Carbon     | 0.010 – 0.100% |
| Manganese  | 0.140 – 0.345% |
| Silicon    | max. 0.06%     |
| Phosphorus | max. 0.025%    |
| Sulfur     | max. 0.030%    |
| Aluminum   | 0.02 – 0.08%   |
| Nitrogen   | max. 0.0080%   |
| Copper     | max. 0.10%     |
| Chromium   | max. 0.10%     |
| Nickel     | max. 0.10%     |
| Boron      | max. 0.006%    |
| Titanium   | max. 0.015%    |

Rest: Iron

### **2. Decarbonized steel (Interstitial-free steel)**

|            |                |
|------------|----------------|
| Carbon     | max. 0.010%    |
| Manganese  | 0.10 – 0.25%   |
| Silicon    | max. 0.15%     |
| Phosphorus | max. 0.020%    |
| Sulfur     | max. 0.020%    |
| Aluminum   | 0.015 – 0.060% |
| Nitrogen   | max. 0.004%    |
| Copper     | max. 0.08%     |
| Chromium   | max. 0.06%     |
| Nickel     | max. 0.10%     |
| Titanium   | 0.02 – 0.10%   |
| Niobium    | max. 0.10%     |

Rest: Iron

### 3. Low-carbon steel

|            |                |
|------------|----------------|
| Carbon     | 0.010 – 0.020% |
| Manganese  | 0.50 – 0.70%   |
| Silicon    | max. 0.06%     |
| Phosphorus | max. 0.025%    |
| Sulfur     | max. 0.020%    |
| Aluminum   | 0.02 – 0.08%   |
| Nitrogen   | max. 0.009%    |
| Copper     | max. 0.12%     |
| Chromium   | max. 0.06%     |
| Nickel     | max. 0.10%     |

Rest: Iron

### 4. Micro-alloyed steel

|            |                 |
|------------|-----------------|
| Carbon     | max 0.10%       |
| Manganese  | max. 1.65%      |
| Silicon    | max. 0.50%      |
| Phosphorus | max. 0.12%      |
| Sulfur     | max. 0.030%     |
| Aluminum   | at least 0.015% |
| Niobium    | max. 0.09%      |
| Titanium   | max. 0.22%      |
| Vanadium   | max. 0.25%      |

Rest: Iron

### 5. Super high-strength, micro-alloyed steel

|            |             |
|------------|-------------|
| Carbon     | max 0.25%   |
| Manganese  | max. 1.65%  |
| Silicon    | max. 0.60%  |
| Aluminum   | min. 0.02%  |
| Phosphorus | max. 0.025% |
| Sulfur     | max. 0.035% |
| Vanadium   | min. 0.03%  |
| Niobium    | min. 0.03%  |
| Molybdenum | min. 0.20%  |

Rest: Iron

(The percentage value designate weight percent).

# ART 34 AMDT

STENGER, WATZKE & RING  
Patent Attorneys

Kaiser-Friedrich-Ring 70  
D-40547 DÜSSELDORF

PCT patent application PCT/EP 00/07503  
Hille & Müller GmbH

Dipl.-Ing. Wolfram Watzke (- 1999)  
Dipl.-Ing. Heinz J. Ring  
Dipl.-Ing. Ulrich Christophersen  
Dipl.-Ing. Michael Rausch  
Dipl.-Ing. Wolfgang Bringmann  
European Patent Attorneys

Our reference: 00-0898  
Your reference:

Date: October 10, 2001

## (Revised) Patent Claims

1. A method for producing improved cold band suitable for drawing or ironing process, with a carbon content of less than 0.5 weight percent, during which the cold band rolled under a cold-rolling ratio of 30 to 95% is subjected to a thermal treatment in an annealing furnace and to a coating procedure, preferably on galvanic basis, on at least one of its surfaces, where the simple or multiple-layer coating contains the elements of nickel / cobalt / iron / bismuth / indium / palladium / gold or their alloys, characterized in that the thermal treatment occurs in
  - the form of annealing of the band in a continual annealing furnace before or after the coating and
  - at a temperature of more than 911°C and, therefore, at any rate above the limit temperature of the two-phase range ferrite / austenite ( $\alpha/\gamma$  range in the iron-carbon system) to austenite range ( $\gamma$  range in the iron-carbon system).
2. A method according to claim 1 characterized in that the coating of the band occurs before the annealing.
3. A method according to claim 1 characterized in that the first coating of the band occurs before the annealing, and that, after the annealing, another coating is deposited on the band, preferably through electroplating, that contains the elements of nickel / cobalt / iron / bismuth / indium / palladium / gold or their alloys.
4. A method according to one of claims 1 to 3 characterized in that, after the annealing, an additional coating of the band occurs using organic ingredients enhancing the brittleness of the coating, where the decomposition products of these organic substances, which are a part of the electrolyte bath, and/or reaction products of organic substances, which are a part of the electrolyte bath, are introduced into the coating.
5. A method according to claim 4 characterized in that the organic ingredients of the electrolyte bath, whose decomposition products and/or reaction products resulting from

— — —  
reactions of these decomposition products with other constituents are introduced into the coating, are brighteners (the so-called primary or secondary brighteners).

6. A method according to one of claims 1 to 3 characterized in that conductive particles consisting, for example, of carbon, carbon black, graphite,  $TaS_2$ ,  $TiS_2$  and/or  $MoSi_2$  are embedded into the coating.
7. A method according to one of claims 1 to 3 characterized in that the coating is covered with a dispersion-hardened coating containing conductive particles such as carbon, carbon black, graphite,  $TaS_2$ ,  $TiS_2$  and/or  $MoSi_2$ .
8. Cold band, preferably for the production of cylindrical containers and especially battery containers by drawing and ironing, consisting of a band rolled under a cold-rolling ratio of 30 to 95%, with a carbon content of less than 0.5 weight percent as well as with a coating applied, preferably in a galvanic process, to at least one of the two surfaces of the band, where the coating contains the elements of nickel / cobalt / iron / bismuth / indium / palladium / gold or their alloys, characterized in that the band is a thermally treated band annealed in a continually annealing furnace at a temperature of more than  $911^\circ C$  and, therefore, at any rate above the limit temperature of the two-phase range ferrite / austenite ( $\alpha/\gamma$  range) to austenite range ( $\gamma$  range).
9. Cold band according to claim 8 characterized in that the band comprises, over the aforementioned coating, at least one more coating consisting of the elements of nickel / cobalt / iron / bismuth / indium / palladium / gold or their alloys.
10. Cold band according to one of claims 8 and 9 characterized in that conductive particles consisting, for example, of carbon, carbon black, graphite,  $TaS_2$ ,  $TiS_2$  and/or  $MoSi_2$  are embedded into the coating.
11. Cold band according to one of claims 8 and 9 characterized in that the coating is covered with a dispersion-hardened coating containing conductive particles such as carbon, carbon black, graphite,  $TaS_2$ ,  $TiS_2$  and/or  $MoSi_2$ .
12. Cold band according to one of claims 8 to 11 characterized by the following composition (besides iron) (in weight percent):

|    |              |
|----|--------------|
| C  | max. 0.3 %   |
| Mn | 0.1 to 2 %   |
| Si | max. 1.0 %   |
| P  | max. 0.25 %  |
| S  | max. 0.06 %  |
| Al | min. 0.015 % |
| N  | max. 0.01 %  |

13. A battery shell characterized in that it is manufactured from a cold band according to one of claims 8 to 12 by a forming process, especially by drawing and ironing.

[Diagram]

Figure 6.6 Iron – carbon diagram

Schmelze +  $\delta$ -Mischkristalle = Molten mass +  $\delta$  mixed crystals

Schmelze +  $\gamma$ -Mischkristalle = Molten mass +  $\gamma$  mixed crystals

Temperatur = Temperature

$\gamma$ -Mischkristalle (Austenit) =  $\gamma$  mixed crystals (austenite)

$\gamma$ -Mischkristalle + Ferrit =  $\gamma$  mixed crystals + ferrite

$\gamma$ -Mischkristalle + Sekundärzementit =  $\gamma$  mixed crystals + secondary cementite

$\alpha$ -Mischkristalle =  $\alpha$  mixed crystals

Ferrit = ferrite

Perlit = perlite

Sekundärzementit + Perlit = Secondary cementite + perlite

Masse = mass

Kohlenstoff = Carbon

#### 6.3.1.1 Structural transformation of unalloyed (plain) steels

If steels are heated to high temperatures, various *transformation points* can be determined. (Figure 6.6). The temperature ranges that contain the transformation points are called transformation ranges. The limits of these ranges change depending on the content of carbon. The transformation points lie on the lines GS, SE, and PSK. The points on the line PSK are called “transformation points” or “A1 points”.

(12) NACH DEM VERTRAG ÜBER DIE INTERNATIONALE ZUSAMMENARBEIT AUF DEM GEBIET DES  
PATENTWESENS (PCT) VERÖFFENTLICHTE INTERNATIONALE ANMELDUNG

(19) Weltorganisation für geistiges Eigentum  
Internationales Büro



(43) Internationales Veröffentlichungsdatum  
15. Februar 2001 (15.02.2001)

PCT

(10) Internationale Veröffentlichungsnummer  
**WO 01/11114 A1**

(51) Internationale Patentklassifikation<sup>7</sup>: **C25D 5/50**

(21) Internationales Aktenzeichen: **PCT/EP00/07503**

(22) Internationales Anmeldedatum:  
3. August 2000 (03.08.2000)

(25) Einreichungssprache: **Deutsch**

(26) Veröffentlichungssprache: **Deutsch/**

(30) Angaben zur Priorität:  
199 37 271.3 6. August 1999 (06.08.1999) DE

(71) Anmelder (*für alle Bestimmungsstaaten mit Ausnahme von US*): **HILLE & MÜLLER GMBH & CO. [DE/DE]; Am Trippelsberg 48, 40589 Düsseldorf (DE)**

(72) Erfinder; und

(75) Erfinder/Anmelder (*nur für US*): **PFEIFENBRING, Karlfried [DE/DE]; Swakopmunder Strasse 18b, 47249 Duisburg (DE). STEINMANN, Hans-Günter [DE/DE]; Otto-Hahn-Strasse 18, 40591 Düsseldorf (DE). SCHMIDT, Ferdinand [DE/DE]; Kammerathsfeldstrasse**

(74) Anwalt: **STENGER, WATZKE & RING; Kaiser-Friedrich-Ring 70, 40547 Düsseldorf (DE)**

(81) Bestimmungsstaaten (*national*): **AU, BR, CA, CN, IL, IN, JP, KR, MX, PL, RU, SG, US**

(84) Bestimmungsstaaten (*regional*): **europäisches Patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE)**

**Veröffentlicht:**

- *Mit internationalem Recherchenbericht.*
- *Vor Ablauf der für Änderungen der Ansprüche geltenden Frist; Veröffentlichung wird wiederholt, falls Änderungen eintreffen.*

*Zur Erklärung der Zweibuchstaben-Codes, und der anderen Abkürzungen wird auf die Erklärungen ("Guidance Notes on Codes and Abbreviations") am Anfang jeder regulären Ausgabe der PCT-Gazette verwiesen.*

(54) **Title:** METHOD FOR PRODUCING IMPROVED COLD ROLLED STRIP THAT IS CAPABLE OF BEING DEEP DRAWN OR IRONED, AND COLD ROLLED STRIP, PREFERABLY USED FOR PRODUCING CYLINDRICAL CONTAINERS AND, IN PARTICULAR, BATTERY CONTAINERS

(54) **Bezeichnung:** VERFAHREN ZUR HERSTELLUNG VON TIEFZIEH- ODER ABSTRECKZIEHFÄHIGEM, VEREDELTEM KALTBAND SOWIE KALTBAND, VORZUGSWEISE ZUR HERSTELLUNG VON ZYLINDRISCHEN BEHÄLTERN UND INSBESONDERE BATTERIEBEHÄLTERN

(57) **Abstract:** The invention relates to a method for producing improved cold rolled strip which is capable of being deep drawn or ironed and which has a carbon content of less than 0.5 wt. %. The invention also relates to a cold rolled strip that can be produced by such a method, preferably used for producing cylindrical containers and, in particular, battery containers by deep drawing or ironing. The strip that is cold rolled with a cold rolling degree ranging from 30 to 95 % is subjected to a thermal treatment in the annealing furnace and to a preferably galvanic coating of at least one of both strip surfaces. In order to obtain an isotropic steel strip which has a low level of texturing and which has a low tendency toward earing, the coating produced with one or multiple layers contains the elements nickel/ cobalt/ iron/ bismuth/ indium/ palladium/ gold/ tin or alloys thereof, whereby the thermal treatment is effected by an annealing, which is carried out before or after the coating process, in the continuously running strip annealing furnace at a temperature greater than the limit temperature to the austenite range ( $\gamma$  range).

A1

(57) **Zusammenfassung:** Vorgeschlagen wird ein Verfahren zur Herstellung von tiefzieh- oder abstreckziehfähigem, veredeltem Kaltband mit einem Kohlenstoffgehalt von unter 0,5 Gew.-%. Vorgeschlagen wird ferner ein durch ein solches Verfahren herstellbares Kaltband, vorzugsweise zur Herstellung von zylindrischen Behältern und insbesondere Batteriebehältern durch Tiefziehen oder Abstreckziehen. Das mit einem Kaltwalzgrad von 30 bis 95 % kaltgewalzte Band wird einer Wärmebehandlung im Glühofen sowie einer vorzugsweise galvanischen Beschichtung zumindest einer der beiden Bandoberflächen unterzogen. Zur Erzielung von texturarmem, isotropem Stahlband mit geringer Neigung zur Zipfelbildung enthält die ein- oder mehrfach erzeugte Beschichtung die Elemente Nickel/ Cobalt/ Eisen/ Wismut/ Indium/ Palladium/ Gold/ Zinn oder deren Legierungen, wobei die Wärmebehandlung durch ein vor oder nach der Beschichtung durchgeführtes Glühen im kontinuierlich durchlaufenden Bandglühofen bei einer Temperatur oberhalb der Grenztemperatur zum Austenitgebiet ( $\gamma$ -Gebiet) erfolgt.

WO 01/11114 A1

01-1467

#4

Practitioner's Docket No. 6171-7

PATENT

**COMBINED DECLARATION AND POWER OF ATTORNEY****(ORIGINAL, DESIGN, NATIONAL STAGE OF PCT, SUPPLEMENTAL, DIVISIONAL,  
CONTINUATION, OR C-I-P)**

As a below named inventor, I hereby declare that:

**TYPE OF DECLARATION**

This declaration is for a national stage of PCT application.

**INVENTORSHIP IDENTIFICATION**

My residence, post office address and citizenship are as stated below, next to my name. I believe that I am an original, first and joint inventor of the subject matter that is claimed, and for which a patent is sought on the invention entitled.

**TITLE OF INVENTION**

METHOD FOR PRODUCING IMPROVED COLD-ROLLED STRIP THAT IS CAPABLE OF BEING DEEP-DRAWN OR IRONED, AND COLD-ROLLED STRIP, PREFERABLY USED FOR PRODUCING CYLINDRICAL CONTAINERS AND, IN PARTICULAR, BATTERY CONTAINERS

**SPECIFICATION IDENTIFICATION**

The specification was filed on August 3, 2000, as International Application Number EP00/07503 and was amended on October 10, 2001.

**ACKNOWLEDGMENT OF REVIEW OF PAPERS AND DUTY OF CANDOR**

I hereby state that I have reviewed and understand the contents of the above-identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose information, which is material to patentability as defined in 37, Code of Federal Regulations, Section 1.56, and which is material to the examination of this application, namely, information where there is a substantial likelihood that a reasonable Examiner would consider it important in deciding whether to allow the application to issue as a patent.

**PRIORITY CLAIM (35 U.S.C. Section 119(a)-(d))**

I hereby claim foreign priority benefits under Title 35, United States Code, Section 119(a)-(d) of any foreign application(s) for patent or inventor's certificate or of any PCT international application(s) designating at least one country other than the United States of America listed below and have also identified below any foreign application(s) for patent or inventor's certificate or any PCT international application(s) designating at least one country other than the United States of America filed by me on the same subject matter having a filing date before that of the application(s) of which priority is claimed.

Such applications have been filed as follows.

**PRIOR FOREIGN APPLICATION(S) FILED WITHIN 12 MONTHS  
(6 MONTHS FOR DESIGN) PRIOR TO THIS APPLICATION  
AND ANY PRIORITY CLAIMS UNDER 35 U.S.C. SECTION 119(a)-(d)**

| COUNTRY | APPLICATION NUMBER | DATE OF FILING<br>DAY, MONTH, YEAR | PRIORITY<br>CLAIMED<br>UNDER 35 U.S.C.<br>SECTION 119 |
|---------|--------------------|------------------------------------|---|
| Germany | 199 37 271.3       | 6 August 1999                      | yes   |

**POWER OF ATTORNEY**

I hereby appoint the following practitioner(s) to prosecute this application and transact all business in the Patent and Trademark Office connected therewith.

| APPOINTED PRACTITIONER(S) | REGISTRATION NUMBER(S) |
|---------------------------|------------------------|
| Stephen L. Grant          | 33390                  |
| Eryn R. Ace               | 44491                  |
| Alexander D. Bonmarito    | 44036                  |
| Robert J. Clark           | 45835                  |
| R. Eric Gaum              | 39199                  |
| Michael H. Minns          | 31985                  |
| Edwin W. Oldham           | 22003                  |
| Scott M. Oldham           | 32712                  |
| Mark A. Watkins           | 33813                  |

I hereby appoint the practitioner(s) associated with the Customer Number provided below to prosecute this application and to transact all business in the Patent and Trademark Office connected therewith.

## SEND CORRESPONDENCE TO

## DIRECT TELEPHONE CALLS TO:

Stephen L. Grant  
330-864-5550

Stephen L. Grant  
1225 W. Market St.  
Akron, OH 44313  
USA

Customer Number 021324

## DECLARATION

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

## SIGNATURE(S)

1 - 00 Karlfried PFEIFFENBRING

Inventor's signature

Date 19.Feb.2002



Country of Citizenship Germany

Residence Duisberg Germany

Post Office Address Swakopmunder Strasse 18b, D-47249 Duisberg Germany

■■■■■

2 - 00 Hans-Guenter STEINMANN

Inventor's signature

Date 27.02.02



Country of Citizenship Germany

Residence Duesseldorf Germany

Post Office Address Otto-Hahn-Strasse 18, D-40591 Duesseldorf Germany

■■■■■

3 - 00 Ferdinand SCHMIDT

Inventor's signature

Date \_\_\_\_\_



Country of Citizenship Germany

Residence Duesseldorf Germany

Post Office Address Kammerathsfeldstrasse 56, D-40593 Duesseldorf Germany

4-00 Werner OLBERDING

Inventor's signature



Country of Citizenship Germany

Date 20.02.2002

Residence Velbert Germany DEX

Post Office Address Am Feldgen 32, D-42553 Velbert Germany



5 - 00 Marcel Sebastian RUBART

Inventor's signature



Country of Citizenship Germany

Date 20.02.02

Residence Dinslaken Germany DEX

Post Office Address Am Stadtbad 56, D-46537 Dinslaken Germany

